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H₂ production by steam reforming with in situ CO₂ capture of biomass-derived bio-oil

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Abstract

High-purity H₂ was produced by the sorption enhanced steam reforming (SESR) of acetic acid, a model compound of bio-oil obtained from biomass fast pyrolysis. A fixed bed reactor comprising two sections with different temperature was used to favor the reforming reaction in the high-temperature section, and the water gas shift (WGS) and the CO₂ capture reactions along the low-temperature segment. A Pd/Ni-Co hydrotalcite-like material (HT) was used as catalyst and a CaO-based material as CO₂ sorbent. High H₂ yield (84.4%), with H₂ purity of 99.8%, was obtained at atmospheric pressure and 600 °C in the above section of the bed followed by a bed temperature of 500 °C at the bottom part. A null CO concentration was achieved, while the CH₄ and CO₂ contents showed very low values (0.15% and 0.02%, respectively).

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Keywords: H₂ production; sorption enhanced steam reforming (SESR); Pd/Ni-Co catalyst; biomass; bio-oil

1. Introduction

Hydrogen is considered as one of the most important potential clean energy carriers for the near future. Over the next few decades, the demand for H₂ is expected to grow exponentially, both for conventional industrial uses and for clean energy generation, particularly in fuel cell applications [1]. H₂ is nowadays mainly produced from fossil fuels by steam methane reforming (SMR) of natural gas or via partial oxidation of heavy oil fractions. These methods produce pure H₂ and CO₂ as a byproduct. The increasing concentration of greenhouse gases in the atmosphere and

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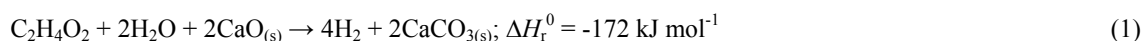
the worldwide recognition of their effect on global climate change have increased the concern on the control of the CO₂ emissions from the energy generation industry, since CO₂ is the greenhouse gas with the largest contribution to climate change.

Several technologies for CO₂ reduction are currently under study and the sorption enhanced steam reforming (SESR) process is becoming an important topic since it integrates hydrogen production and CO₂ separation. During the SESR process, carbon dioxide is captured by an *in situ* sorbent, shifting the reversible reforming and water gas shift (WGS) reactions to the product side beyond their conventional thermodynamic limits, which increases the H₂ concentration in the gas produced and allows almost complete conversion to be achieved. Captured CO₂ is converted to a solid carbonate if a CaO-based sorbent is used. This sorbent can be regenerated to release relatively pure CO₂ suitable for storage. The SESR process can be carried out at much lower reaction temperatures than the conventional reforming processes, which would reduce catalyst coking and sintering, as well as investment and operation costs. In addition, heat released by the exothermic carbonation reaction supplies most of the heat required by the endothermic reforming reactions. However, energy will be required to regenerate the sorbent by the energy-intensive calcination reaction.

The full environmental benefit of the hydrogen application as an energy carrier can only be reached if hydrogen is produced from renewable sources, such as biomass [2]. Biomass offers the best route for accelerating the introduction of green hydrogen as a major fuel in the future, since biomass does not contribute to a net increase in atmospheric CO₂. H₂ produced from biomass is considered CO₂ neutral because the equivalent quantity of CO₂ evolved during biomass conversion is removed from the atmosphere via photosynthesis. Furthermore, the coupling of biomass conversion technologies with CO₂ capture and storage technologies offers the potential to achieve an effective reduction in CO₂ from the atmosphere [3].

H₂ can be produced from biomass using routes with intermediate steps of production of oxygenates, which are subsequently reformed. Flash pyrolysis is an attractive method to produce pyrolysis oil (bio-oil) from different types of biomass, which will be later treated by catalytic reforming to obtain hydrogen. Bio-oil is a complex mixture of a large number of compounds, including acids, aldehydes, alcohols, ketones, phenols and sugars. The aqueous carbohydrate-derived fraction of the bio-oil can be steam reformed for hydrogen production. Acetic acid is one of the most representative constituents of the water soluble fraction of bio-oils and it is used as a model compound of bio-oil produced by the fast pyrolysis of biomass. Several works on hydrogen production by conventional steam reforming of bio-oil compounds have been reported in the literature [4-9], but the sorption enhanced concept has not been extensively studied.

The overall reaction for the sorption enhanced steam reforming (SESR) process of acetic acid is shown in Eq. (1), which is a combination of the steam reforming, water gas shift and CO₂ capture reactions.



Typical operating temperatures in the SESR process at atmospheric pressure are between 400 and 650 °C. This process therefore requires the use of very active and stable reforming catalysts. The main functions required for the catalyst are a high activity and selectivity towards H₂ and CO formation, through the cleavage of C-C and C-H bonds, and a high catalytic activity in the high-temperature WGS reaction. It has been showed that a Ni-Co catalyst derived from a hydrotalcite-like material (HT), used with dolomite as CO₂ sorbent, is very effective in enhancing hydrogen production and purity in the SESR process with biomass-derived compounds, such as syngas [10], glycerol [11, 12], ethanol [13] and glucose [14]. Moreover, an improved Pd/Ni-Co HT catalyst has recently been successfully employed to produce a high H₂ yield of great purity from biomass-derived compounds [15]. This catalyst will be used in the present study. Furthermore, although the SESR process could significantly enhance the hydrogen production in relation to the conventional steam reforming, the process operation variables need to be evaluated and optimized in order to maximize the H₂ production.

The objective of the present study was to investigate the effect of the reaction temperature and pressure on the H₂ production by the sorption enhanced steam reforming of acetic acid over a Pd/Ni-Co hydrotalcite-derived catalyst and using dolomite as CO₂ sorbent material. A bench-scale fixed bed reactor comprising two sections able to work at different temperature was used in order to favor the reforming reaction in the high-temperature section, and the water gas shift and CO₂ capture reactions along the low-temperature segment, aiming at a very low CO

concentration in the effluent gas. H_2 yield, H_2 selectivity and H_2 purity, as well as CH_4 , CO and CO_2 concentrations in the effluent gas were determined. Thermodynamic equilibrium analysis of the process was carried out in order to assess the theoretical feasibility of the process at the studied reaction conditions and to compare the equilibrium values with the experimental results.

2. Experimental

2.1. Feedstock and CO_2 sorbent

Acetic acid was selected as an oxygenated model compound of organic acids contained in the aqueous phase of bio-oils produced by the fast pyrolysis of biomass. Glacial acetic acid was supplied by PANREAC (100% purity). An aqueous solution of acetic acid was prepared using a water-to-acetic acid molar ratio of 6 (steam/C molar ratio of 3). Arctic dolomite, used as a precursor of CaO for the capture of CO_2 , was supplied by Franefoss Miljøkalk AS, Norway. This had a purity of 98.5 wt.% $CaMg(CO_3)_2$ and no sulfur according to X-ray fluorescence analysis. The dolomite sample was calcined in an air flow at 770 °C for 4 h prior to its application as CO_2 sorbent. The initial maximum CO_2 capture capacity was estimated as being 0.46 g CO_2 /g sorbent.

2.2. Catalyst preparation

The 1%Pd/20%Ni-20%Co HT catalyst (Pd/Ni-Co HT) used in the present work was prepared by the incipient wetness impregnation method using a 20%Ni-20%Co hydrotalcite-like material (Ni-Co HT) as precursor. The Ni-Co HT precursor was prepared by co-precipitation of $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_3 \cdot 6H_2O$, $Mg(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$. A stoichiometric ratio of cations was chosen to achieve a 40 wt.% total metal load of Ni and Co, resulting in a material with nominal composition of 20%Ni-20%Co. The precipitate obtained was filtered, washed, dried overnight and then calcined at 600 °C for 6 h. A detailed description of the precursor preparation procedure has been reported elsewhere [16]. After calcination, the Ni-Co HT precursor was impregnated with a 1% (w/w) load of Pd. The Pd solution was prepared by dissolving $PdCl_2$ into two equivalents of HCl and diluting them in ethanol to the desired concentration. The sample was then dried for 14 h at 100 °C and calcined in an air flow at 500 °C (heating rate of 5 °C min^{-1}) for 1 h in a muffle oven. The calcined catalyst was pelletized, ground and sieved to the desired particle size (250-500 μm). A detailed description of the Pd/Ni-Co HT catalyst preparation procedure has been reported elsewhere [15].

2.3. Experimental procedure

The schematic diagram of the experimental setup used for the SESR experiments with acetic acid is shown in Fig. 1. It consists of a downdraft fixed bed stainless steel reactor (13 mm internal diameter, 305 mm height), which was loaded with a 12 g mixture of calcined dolomite (as CO_2 sorbent) and Pd/Ni-Co HT catalyst, at a sorbent-to-catalyst ratio of 5 g/g. SESR experiments were carried out at 1 and 15 atm and isothermally at temperatures between 550 and 900 °C in the upper section of the reactor, i.e. the high-temperature segment. The temperature of the lower zone was 100 °C below the temperature of the upper part. Thus, the upper part of the catalyst/sorbent bed (70 mm) was maintained at the highest temperature, whereas the lower part of the bed (40 mm) was kept at the lowest temperature during the reforming experiments. The gases were delivered by Bronkhorst® mass flow controllers. Prior to each SESR experiment, the catalyst/sorbent mixture was subjected to a regeneration step at 770 °C in an air flow (200 $NmL min^{-1}$) until the CO_2 level fell to less than 0.1 vol.%. The temperature of 770 °C was selected from preliminary experiments, taking into consideration the thermodynamic limitations of the decarbonation reaction and the kinetics of the decarbonation of dolomite [13]. A regenerated catalyst/sorbent mixture was used in all the SESR experiments in the present study. After regeneration, the reactor was purged with N_2 and cooled down to the desired experimental reaction temperature. The reaction temperatures were controlled by type K thermocouples inserted into the catalyst/sorbent bed. Once the operating temperatures were reached under N_2 atmosphere, the liquid reactant mixture (steam/C = 3) was swept by a 20 $NmL min^{-1}$ N_2 flow (used as internal standard), evaporated in an evaporator and then introduced downdraft through the catalyst/sorbent bed at a total liquid flow rate of 5.0 g h^{-1} . The aqueous

solution of acetic acid was fed in by means of a Gilson® high-performance liquid chromatography (HPLC) pump. The SESR of acetic acid proceeded until the CO₂ sorbent (calcined dolomite) became saturated and lost its capacity for CO₂ removal. Afterwards, CO₂ capture by the sorbent was negligible and a conventional steam reforming (SR) process was assumed to occur.

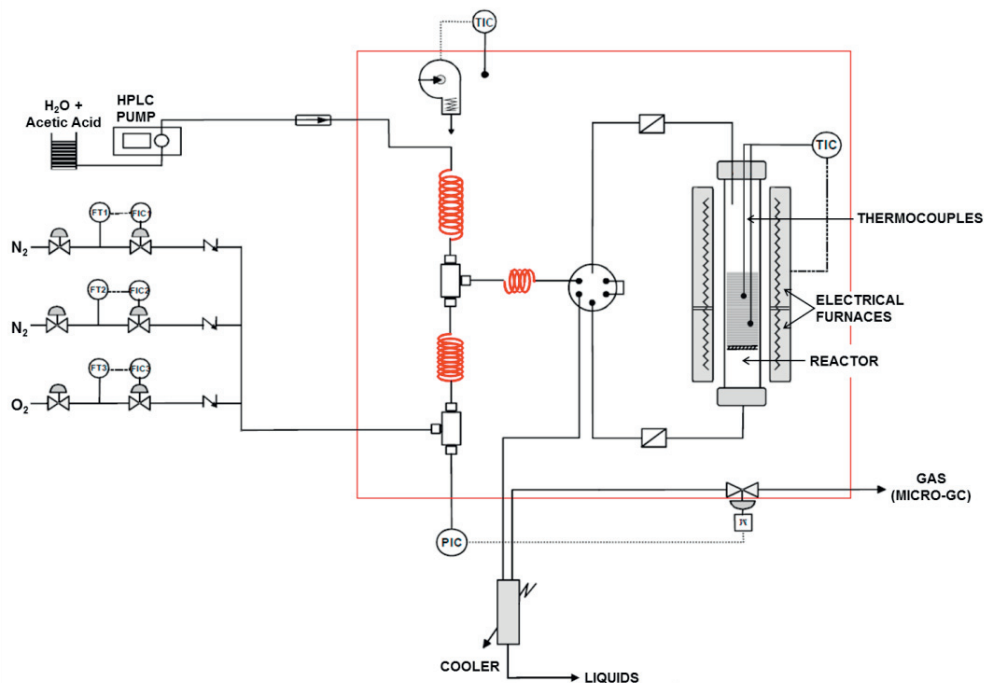


Fig. 1. Schematic flow diagram of the experimental setup used for the SESR experiments with acetic acid.

The effluent gas from the reactor was directed into a thermoelectric cooler, where steam excess, unreacted acetic acid and all other liquids that may have been formed were condensed. The composition of the dried gas was analyzed using an on-line dual channel Varian® CP-4900 Micro GC, equipped with both molecular sieve (Molsieve 5 Å) and HayeSep A columns, and with a thermal conductivity detector (TCD). Helium was used as the carrier gas. The species detected were H₂, CH₄, CO, and CO₂. The product distribution was calculated on the basis of the dry composition of the gas effluent. The flow rates of the species generated during the experiment were calculated by means of a nitrogen balance, since the amount of nitrogen fed in and the composition of the nitrogen evolved are known.

The H₂ yield, H₂ selectivity, H₂ purity and the CH₄, CO, and CO₂ concentrations were calculated from Eq. (2)-(5), respectively:

$$\text{H}_2 \text{ yield (\%)} = 100 \cdot (F_{\text{H}_2} / 4 \cdot F_{\text{acetic acid}}) \quad (2)$$

$$\text{H}_2 \text{ selectivity (\%)} = 100 \cdot [2 \cdot y_{\text{H}_2} / (2 \cdot y_{\text{H}_2} + 4 \cdot y_{\text{CH}_4})] \quad (3)$$

$$\text{H}_2 \text{ purity (vol.\%)} = 100 \cdot (y_{\text{H}_2} / \sum_i y_i) \quad (4)$$

$$\text{CH}_4/\text{CO}/\text{CO}_2 \text{ (vol.\%)} = 100 \cdot (y_{\text{CH}_4/\text{CO}/\text{CO}_2} / \sum_i y_i) \quad (5)$$

where F_{H_2} is the molar flow rate of the H_2 produced (mol min^{-1}), $F_{\text{acetic acid}}$ is the molar flow rate of the acetic acid fed in (mol min^{-1}), and y_i is the molar content (N_2 free and on a dry basis) of each species i (H_2 , CH_4 , CO and CO_2). The weight hourly space velocity (WHSV) is defined as the ratio of the mass flow rate of the inlet acetic acid to the mass of catalyst ($\text{g}_{\text{acetic acid}} \text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$).

2.4. Thermodynamic equilibrium calculations

Thermodynamic analysis of the SESR process was conducted under the reaction conditions studied. The equilibrium composition was estimated by minimizing the Gibbs free energy. Aspen Plus 7.2 software (Aspentech) was used for the calculations. The RGibbs reactor was specified as the reaction system. The Peng-Robinson property method was used to predict the thermodynamic behavior of the system. According to the results obtained for the prediction of the equilibrium under sorption enhanced conditions, the species produced in concentrations higher than 10^{-4} mol% were H_2 , CO , CO_2 , CH_4 , H_2O , CaO and $CaCO_3$. C_2H_4 , C_2H_6 and C (graphite as solid carbon) were also included in the product pool, but their concentrations in the equilibrium stream were null or not high enough to be considered as significant products [13]. The product mole fractions were calculated on a dry basis.

3. Results and discussion

Fig. 2 shows the results for H_2 yield (Fig. 2a), H_2 selectivity (Fig. 2b) and H_2 purity (Fig. 2c). Fig. 3 shows the results for CH_4 (Fig. 3a), CO (Fig. 3b) and CO_2 (Fig. 3c) concentrations. In all the plots, the points represent the experimental results, whereas the lines show the equilibrium values obtained from the thermodynamic analysis.

During the SESR process of acetic acid (blue and red points) it can be seen that the H_2 yield (Fig. 2a) increased slightly with temperature up to a maximum value, after which their values decreased. H_2 yield reached its maximum value at 650–700 °C at atmospheric pressure (and around 800 °C at 15 atm) and then slightly decreased. High values of H_2 purity (Fig. 2c) were obtained up to approximately 700 °C at atmospheric pressure (and 800 °C at 15 atm), but they then markedly decreased. H_2 selectivity (Fig. 2b), CO concentration (Fig. 3b) and CO_2 concentration (Fig. 3c) increased as temperature increased, whereas CH_4 concentration (Fig. 3a) decreased. With increasing temperature, the methanation reaction becomes thermodynamically unfavorable and steam methane reforming is kinetically enhanced, which results in lower CH_4 concentration, although the CH_4 content showed low values during the SESR stage at all the temperatures studied in the present work. This indicated that the Pd/Co-Ni HT catalyst successfully catalyzed the methane steam reforming reaction.

At atmospheric pressure, temperatures higher than 750 °C during the SESR process caused a significant decrease in H_2 purity (Fig. 2c) as well as an important increase in the CO and CO_2 contents (Figs. 3b and 3c). Similar results were obtained at 15 atm when temperature was higher than approximately 800 °C. The lower CO concentration found at lower temperatures can be explained by the favorable thermodynamics of the WGS reaction at low temperatures. Likewise, the CO_2 concentration decreased with decreasing temperature due to the favorable thermodynamics of the carbonation reaction at low temperatures. This led to a very weak sorption enhancement at temperatures higher than 700 °C at atmospheric pressure (or 800 °C at 15 atm), reflected in higher CO_2 concentrations under these conditions. Furthermore, since the CO_2 sorption led to an enhanced H_2 production by shifting the equilibrium of the steam reforming and WGS reactions, lower values of the H_2 purity and higher CO concentrations were observed at high temperature conditions.

On the other hand, at atmospheric pressure the H_2 yield, H_2 selectivity, CO and CO_2 concentrations obtained were higher than those for 15 atm. This difference decreased as temperature increased in the case of the H_2 yield and H_2 selectivity (Figs. 2a and 2b), whereas it became much higher at higher temperatures in the case of the CO and CO_2 concentrations (Figs. 3b and 3c). H_2 purity (Fig. 2c) was higher at atmospheric pressure until approximately 700 °C, but their values were higher at 15 atm at higher temperatures. Moreover, the difference between the results became much higher as temperature increased, since H_2 purity obtained at 1 atm drastically decreased when temperature increased approximately above 750 °C. Finally, CH_4 concentrations (Fig. 3a) obtained at atmospheric pressure were lower than those for 15 atm, but the difference became lower as temperature increased.

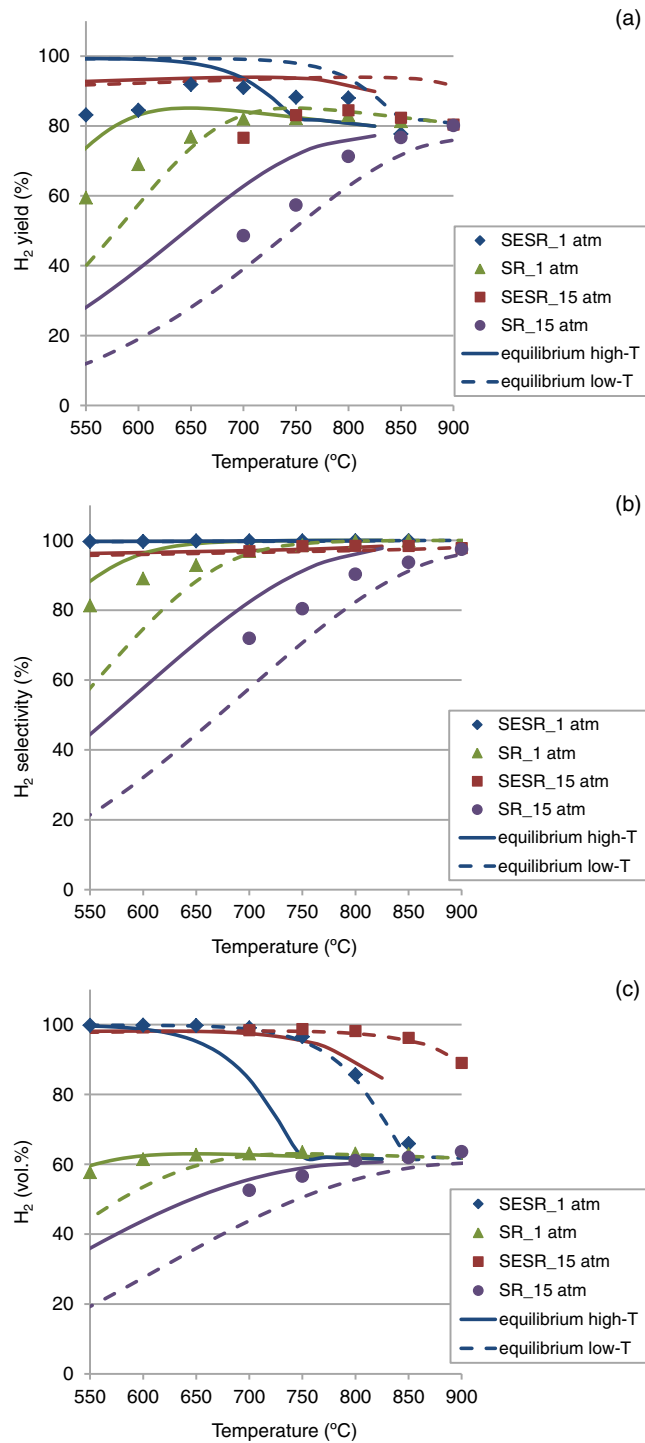


Fig. 2. Effect of the reaction temperature and pressure during the SESR process of acetic acid on H₂ yield (a), H₂ selectivity (b) and H₂ purity (c). Reaction conditions: steam/C=3 mol/mol; WHSV=0.89 h⁻¹; sorbent/catalyst ratio=5 g g⁻¹ and dolomite as sorbent.

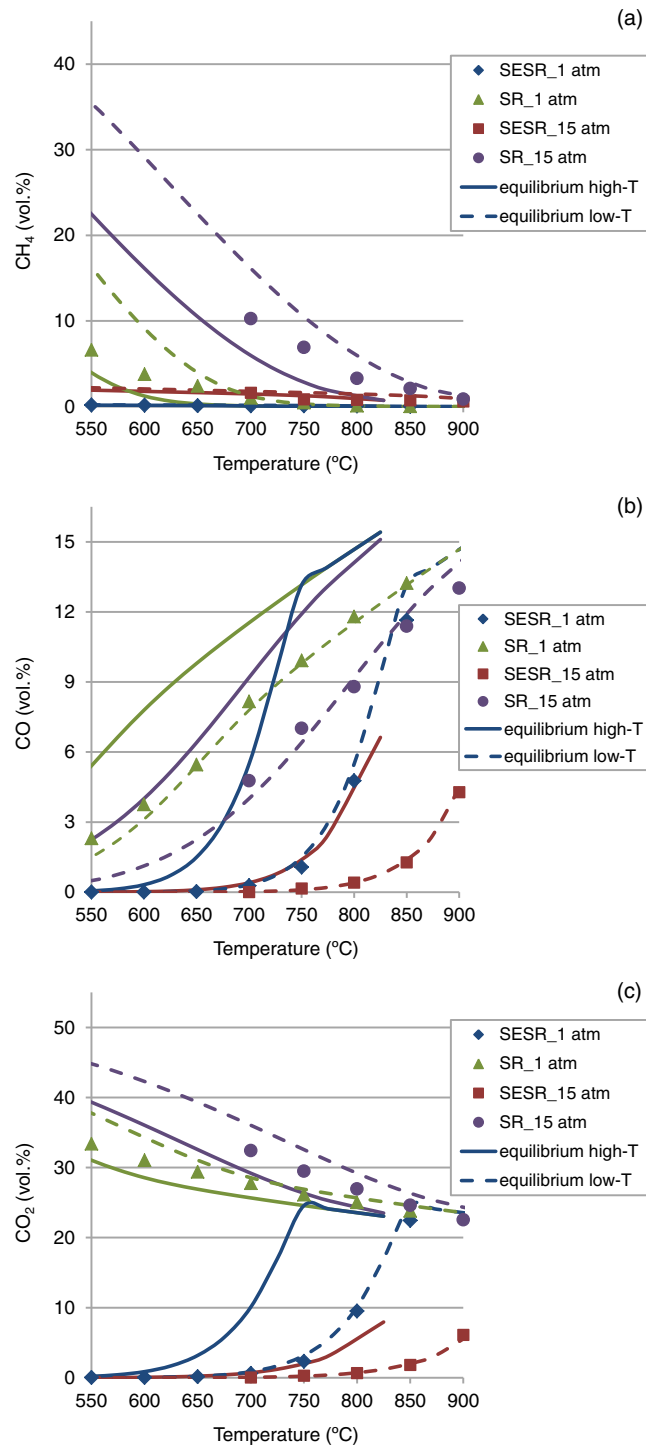


Fig. 3. Effect of the reaction temperature and pressure during the SESR process of acetic acid on the product gas composition (N₂ free and dry basis): (a) CH₄, (b) CO and (c) CO₂. Reaction conditions: steam/C=3 mol/mol; WHSV=0.89 h⁻¹; sorbent/catalyst ratio=5 g g⁻¹ and dolomite as sorbent.

During the SR stage of the process (green and purple points), the H_2 yield, H_2 selectivity, H_2 purity and CO concentration increased with temperature. Their values at atmospheric pressure were higher than those obtained at 15 atm. However, CH_4 and CO_2 concentrations decreased as temperature increased, and their values were higher at 15 atm than at atmospheric pressure.

Figs. 2 and 3 also show the equilibrium values corresponding to the temperature in the upper section of the reactor, i.e., equilibrium high-T (continuous lines), as well as the equilibrium values calculated at the temperature maintained in the lower segment of the reactor, i.e., equilibrium low-T (dashed lines). The experimental values will be compared with those in the equilibrium. The X-axis in Figs. 2 and 3 shows the temperature of the upper segment of the bed (higher temperature).

Taking into account the SESR stage (blue and red points), it can be observed that H_2 yield values (Fig. 2a) at high temperatures (in the case of atmospheric pressure) were higher than those of the equilibrium high-T (continuous lines). However, the H_2 yield followed quite well the trend of the equilibrium low-T lines (dashed lines), although their values were slightly below those corresponding to the equilibrium of the lower temperature of the reactor. H_2 purity values (Fig. 2c) were higher, whereas CO and CO_2 concentrations (Figs. 3b and 3c) were lower than those of the equilibrium high-T (continuous lines). However, these values followed quite accurately the lines corresponding to the equilibrium low-T (dashed lines). This indicated that when the temperature decreased along the lower segment of the reactor, the CO_2 capture increased and CO was also converted by WGS, which decreased their concentrations and then increased the H_2 content. Furthermore, the reforming process was still favored in the low temperature segment of the reactor due to the capture of CO_2 , which could have contributed to the increase in the H_2 purity.

If the SR stage is considered (green and purple points), the low temperature in the lower segment of the reactor favored the CO conversion by the WGS reaction, but not the reforming reaction. In fact, the equilibrium concentrations of H_2 for SR at low temperatures were very low (dashed lines). Fig. 2c seems to indicate that the reforming reaction (SR) occurred in the upper part of the reactor where the temperature was high enough, but it is probable that the equilibrium concentrations corresponding to that temperature were not reached. This seems to be confirmed because the CH_4 concentrations were slightly above the high-T equilibrium values (Fig. 3a). However, as the temperature was reduced in the lower part of the reactor, the WGS was favored and the consumption of CO was promoted. Then, the experimental CO concentrations during the SR stage were very close to those of the equilibrium low-T. It also would have increased the H_2 purity, as it can be observed in Fig. 2c, which then effectively reached the equilibrium high-T values. In the case of the H_2 yield, H_2 selectivity, CH_4 and CO_2 concentrations, the experimental values for both 1 and 15 atm were in a half-way point between both equilibrium lines, which indicated that the low temperature step in the lower section of the reactor helped to approximate the equilibrium values corresponding to the temperature in the upper part of the reactor.

The experimental values for the SESR stage indicated that the maximum value of H_2 purity that can be experimentally obtained within the range under study was 99.8%. This value was obtained at a temperature of 600 °C in the upper section of the reactor (500 °C in the lower region of the reactor). Under such conditions, the H_2 yield and H_2 selectivity values obtained were 84.5% and 99.7% respectively. Likewise, the CH_4 , CO and CO_2 concentrations were 0.15%, 0% and 0.02%, respectively. The H_2 yield and H_2 selectivity could be increased if the temperature in the upper section of the reactor was increased up to 650 °C, reaching values of 91.9% and 99.8%, respectively. CH_4 concentration would also decrease up to 0.10%. However, under such conditions, the H_2 purity would decrease up to 99.7% and the CO and CO_2 concentrations would increase up to 0.02% and 0.14%, respectively. Therefore, if the objective of the SESR process carried out under two steps with different temperature would be to minimize the CO concentration in the effluent gas, then the optimum temperature in the upper section of the reactor has to be 600 °C, with a temperature of 500 °C in the lower region of the reactor.

4. Conclusions

The sorption enhanced steam reforming (SESR) of acetic acid for H_2 production was performed by using a Pd/Ni-Co hydrotalcite-derived catalyst and a CaO-based material as CO_2 sorbent. The utilization of a fixed bed reactor with two sections of different temperature favored the reforming reaction in the upper high-temperature section, and the water gas shift and the CO_2 capture reactions in the low-temperature segment in the lower part of the reactor. Thus, during the SESR stage, the equilibrium values corresponding to the low temperature of the lower section of the

reactor were reached for all the variables studied, except for the H₂ yield, which attained values slightly lower than those for the equilibrium at low-T but higher than those for the equilibrium at high-T. During the SR stage, the H₂ purity reached the equilibrium values corresponding to the high temperature of the upper section of the reactor, whereas the CO concentration attained the equilibrium values corresponding to the low temperature of the lower section of the reactor. The rest of the variables showed experimental values in a half-way point between both equilibrium lines. The results of the present work showed that the SESR process can be successfully employed for the production of H₂ with high yield (84%) and purity (99.8%) with null CO content in effluent gas from bio-oil at atmospheric pressure and 600 °C in the above section of the bed, followed by a bed temperature of 500 °C at the bottom part of the reactor. Therefore, the steam reforming with in situ CO₂ capture process is presented as a promising technology for the production of high-purity hydrogen from biomass-derived compounds.

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